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SYNTHESIS OF HYDROPHILIC POLYPYRROLE THIN FILMS BY SILAR METHOD

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Abstract. Hydrophilic polypyrrole (PPy) thin films were deposited by simple Successive Ionic Layer Adsorption and Reaction (SILAR) method on glass and stainless steel substrate from aqueous solution. The structural and optical properties were studied by means of X-ray diffraction (XRD), Fourier transforms infrared (FTIR) spectroscopy, and Fourier transforms Raman (FT-Raman) Spectroscopy and UV–VIS spectrophotometer. The surface wettability properties were studied by means of Contact angle meter. The results showed the SILAR method allows the formation of amorphous and hydrophilic polypyrrole thin films. The polypyrrole thin film showed contact angle of in the range of θ_c = 30 deg. to θ_c = 48 deg. The calculated value of surface tension varies between 11.68 mN/m and 19.60 mN/m. Also, the values for work of adhesions were calculated.

1. Introduction

Recently, hydrophilic surfaces have proved that superiority in the myriad applications such as electrochemical double layer capacitance, gas sensing etc. Generally, the hydrophilicity and hydrophobocity is divided into four types and it depends on the contact angle. If the contact angle θ_c<5 deg. then the surface is superhydrophilic, if $90<\theta_c>5$ deg.then surface is hydrophilic, if $160<\theta_c>90$ deg. then surface is hydrophobic and if $\theta_c > 160$ deg. then surface is superhydrophilic. The surface wettability property of solid surface with liquid surface is totally dependent on the dynamics of contact angle.

Now a day, researchers have interested in the polymer types of materials particularly, in the conducting polymers. Conducting polymers are called conjugated polymers as well as synthetic metals. Most studied conducting polymers are polyaniline (PAni), Polypyrrole (PPy) and Polythiophene (PTh) etc., because of the easy synthesis and environmental stability. Among these conjugated polymers, PPy have hugely studied because variety of synthesis condition and highly conducting than others.

Basically, the polymers of pyrrole have synthesized by chemical methods [1] and electrochemical synthesis [2, 3], out of which chemical methods have highly recommended than electrochemical methods because the final product is in large proportion than the final product obtained by electrochemical methods. The schematic presentation of preparation of Polypyrrole (PPy) by chemical polymerization methods is represented in the Fig. 1, which shows that the mechanism of polymerization. Monomer and oxidant with suitable electrolyte form the intermediate species with time such as oligomers, dimmers, trimers and finally polymer chain with linked monomer with alternate single and double bonds, so called the conjugated polymers. No more results were found in the literature on the surface wettability properties of chemically synthesized polypyrrole thin films. More efforts have been taken on the synthesis of polypyrrole thin films by both chemical synthesis methods. Here we choose the simple, less expensive and room temperature based SILAR method for synthesis of polymer. And we studied the surface wettability property.

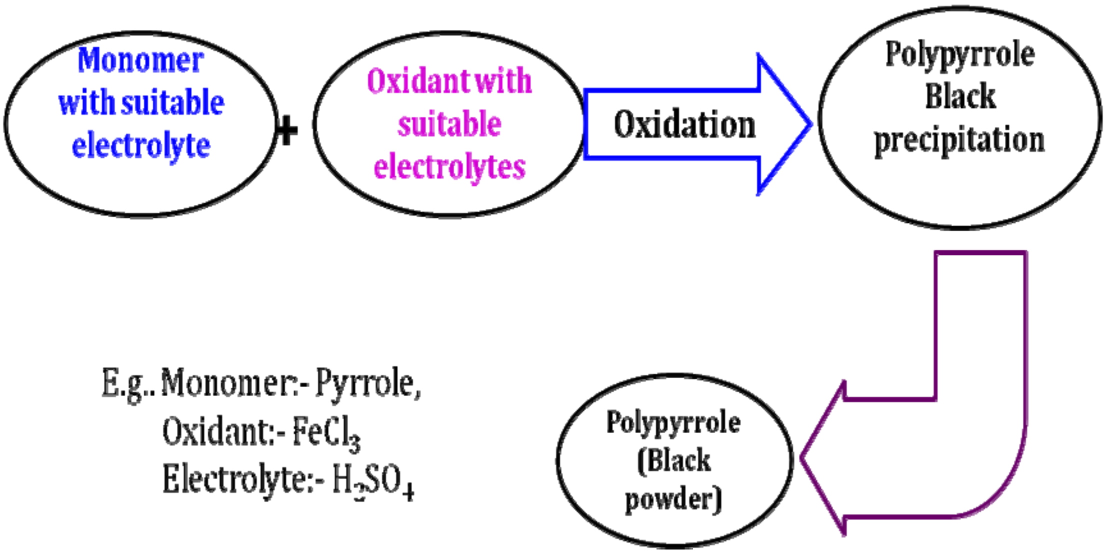

Fig. 1. Schematic presentation of Chemical Polymerizations of Polypyrrole (PPy).

In the present work, we prepared the PPy thin films by simple, inexpensive SILAR method. The PPy thin films were deposited on the stainless steel and glass substrate. After deposition, films were rinsed with distilled water to remove the residue (or monomer free). Further the films were characterized by XRD, FTIR, FT-Raman and UV-VIS spectroscopy. Surface wettability study and some related parameters were calculated from the contact angle measurement.

2. Experimental

2.1. Chemicals. The pyrrole was obtained from SPECTROCHEM PVT., LTD., Mumbai. Ammonium per sulphate (APS) was obtained from SPECTROCHEM PVT., LTD., Mumbai and used as received without any further purification. H_2SO_4 were obtained from SDFL, PVT., LTD., Mumbai. For contact angle measurement, we were used the double distilled water.

2.2. Preparation of PPy film. Hydrophilic Polypyrrole (Ppy) thin films were deposited by simple successive ionic layer adsorption and reaction (SILAR) method on glass and stainless steel substrate from aqueous solution. The growth of Polypyrrole thin films was carried out by the SILAR method at room temperature. The SILAR method consists of two (or more than two) chemical baths. Polypyrrole film was prepared from the oxidation of 0.1 M solution of pyrrole dissolved in 50 mL of 0.1 M H_2SO_4 (I^{st} chemical bath)and 0.1 M Ammonium per sulphate (APS) dissolved in 50 mL of 0.1M H_2SO_4(II^{nd} chemical bath). Schematic presentation of SILAR method is shown in Fig. 2. The 0.1M ammonium per sulphate in 50 mL of 0.1 M H_2SO_4 solution was used as a cationic and 0.1M pyrrole in 50 mL of 0.1 M H_2SO_4 solution was used as an anionic precursors. One SILAR cycle consists of two steps: (1) adsorption of pyrrole cations for 10 s, (2) reaction with ammonium per sulphate precursor solution for 10 s to form stable Polypyrrole. The higher concentration of precursor solutions resulted in to a higher growth rate but the quality of the film was poor due to powdery deposit. In order to prepare monomer free deposited film, after complete deposition, the deposited films were rinsed with double distilled water.

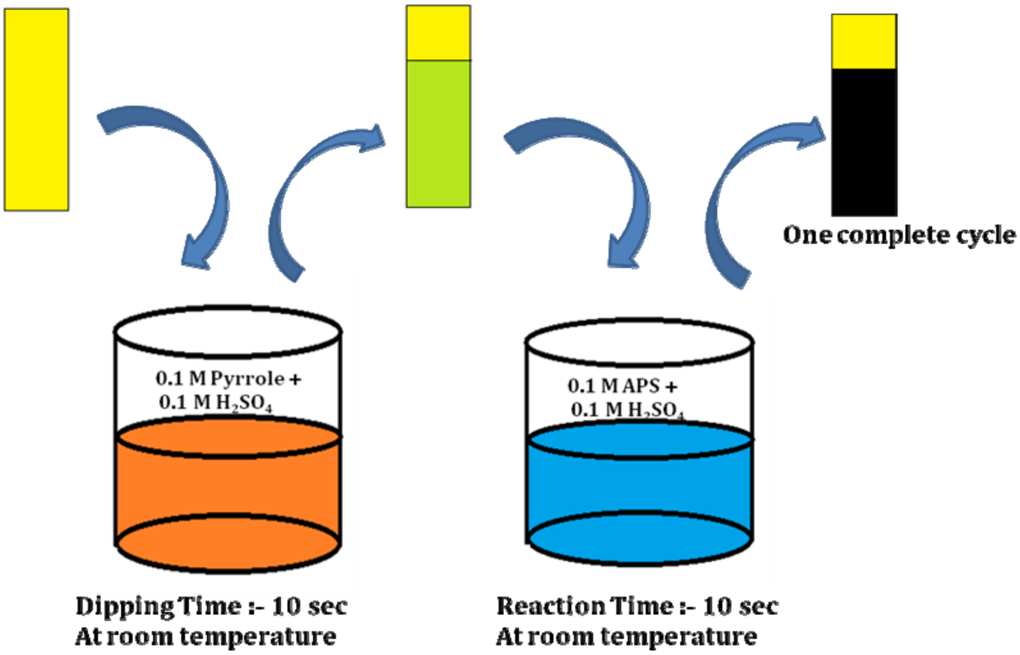

Fig. 2. SILAR method based Polypyrrole synthesis

2.3. Characterization. The chemically polymerized films were characterized by different physico and chemical methods. Thickness measurement was carried out with the help of surface profiler. The structural study was made with the help of X-ray diffraction (a Bruker D8-Focus diffractometer (XRD) operating with a Cu Kα radiation source filtered with a graphite monochromator (λ=1.5406 Å)) and FTIR spectroscopy was studied with the Fourier transform infrared spectrum (FT-IR), which was recorded between 4000 and 450 cm^{-1} at a spectral resolution of 2 cm^{-1} on a Perkin–Elmer 1710 spectrophotometer. UV-VIS absorption study was made using a 119 SYSTRONICS UV–Vis spectrophotometer. The FT-Raman spectrum was recorded with the help of FT-Raman spectrometer. For contact angle measurement, a water droplet of about 10 μL was placed on the surface of hydrophilic polypyrrole thin films using micro syringe. Static contact angles (θ) of polypyrrole thin films were measured from a water drop placed on the sample surface using Rame–Hart contact angle meter.

3. Results and discussion

3.1. Thickness measurement. Thickness measurement of deposited polypyrrole thin films was measured with the help of surface profiler. Fig. 3 shows the polypyrrole film thickness variation with number of deposition cycles. The rate of increase in the thickness is nonlinear, which has been attributed to the growth by nucleation and oligomer formation process and/or pyrrole radical anions. More nucleation sites contribute to polymerization during the growing procedure. Furthermore, slight decrease in film thickness observed could be attributed to the formation of outer overgrowth particles layer which may develop stress to cause elimination, resulting in peeling off the film after the film reaches at maximum thickness. We got the maximum thickness of 2500 A^0 at 20 deposition cycles.

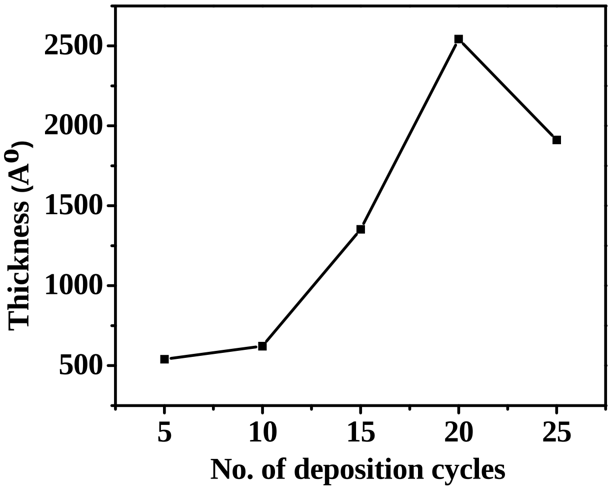

Fig. 3. Variation of film thickness with no. of deposition cycles.

3.2. X-Ray diffraction studies. Figure 4 shows the XRD patterns of PPy thin film. The spectra of polypyrrole don't show any characteristic broad peak. Observed peaks are due to stainless steel substrate only. The XRD patters confirms that the amorphous nature of the chemically deposited polypyrrole thin film.

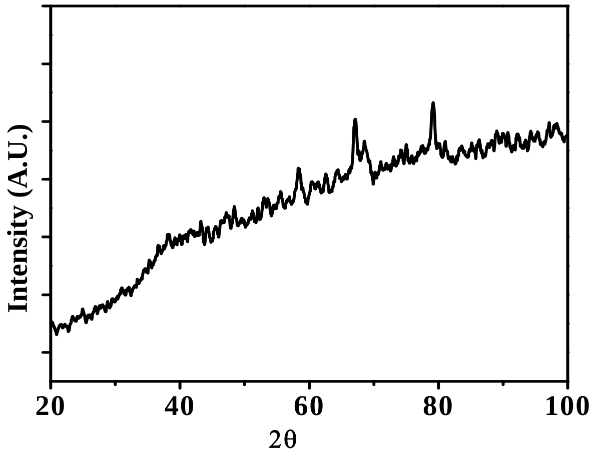

Fig. 4. X-ray diffraction study of Polypyrrole thin films on stainless steel substrate.

3.3. FTIR Spectroscopy. Figure 5 shows the FTIR spectra of PPy thin film. The powders collected from the deposited films were characterized by Fourier-transform infrared (FTIR) measurements (Perkin Elmer IR spectrometer) in the range 400–4000 cm^{-1}.The FTIR spectrogram showed that the strong absorption band at 3430 cm^{-1}, which is attributed to the N–H stretching vibration of polypyrrole, the peak at 1093cm−1 corresponds to in-plane deformation vibration of N^+H_2 [1,5]. The absorption bands at 1535 and 1454 cm^{-1} were associated with the C–C and C–N stretching of the pyrrole ring [5]. The absorption band at 2923 cm^{-1} and 2853 cm^{-1} refers to the stretching vibration of C–H bond. The bands at 1565 cm^{-1} (2, 5- substituted pyrrole) and 1462 cm^{-1} may be assigned to typical Ppy ring vibrations. Transmittance peaks 1171 cm^{-1} band was assigned to N–C stretching band [6].

The peaks at 1546 and 1460 cm^{-1} are attributed to the antisymetric and symmetric pyrrole ring vibrations. The peaks at 1307 and 1047 cm^{-1} are ascribed to in-plain C–H deformation and in-plain N–H stretching vibrations, respectively. The peak at 1310 cm^{-1} is responsible for N-H deformation vibration [7]. The strong peaks at 1172 and 913 cm^{-1} demonstrate the doping state of PPy. The bonds at 966, 678 and 794 cm^{-1} present C–C and C–H out of plane ring deformation vibrations [4].

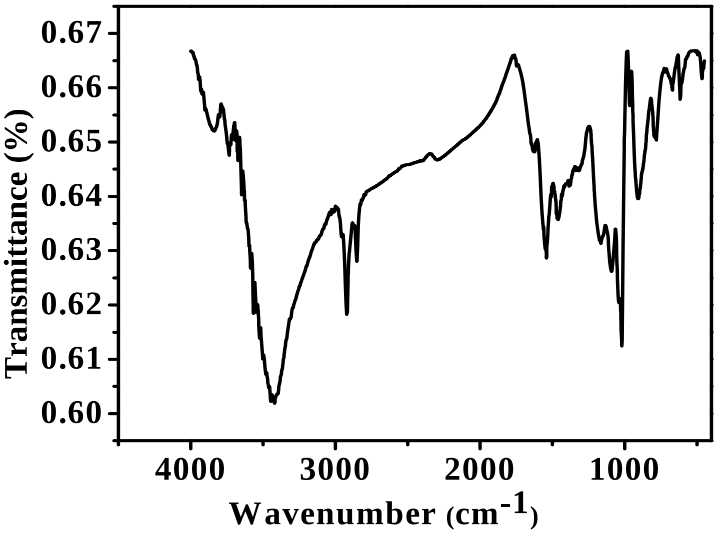

Fig. 5. FTIR spectroscopy of Polypyrrole thin film.

3.4. FT-Raman Spectroscopy. Figure 6 shows the FT-Raman spectra of PPy thin film.

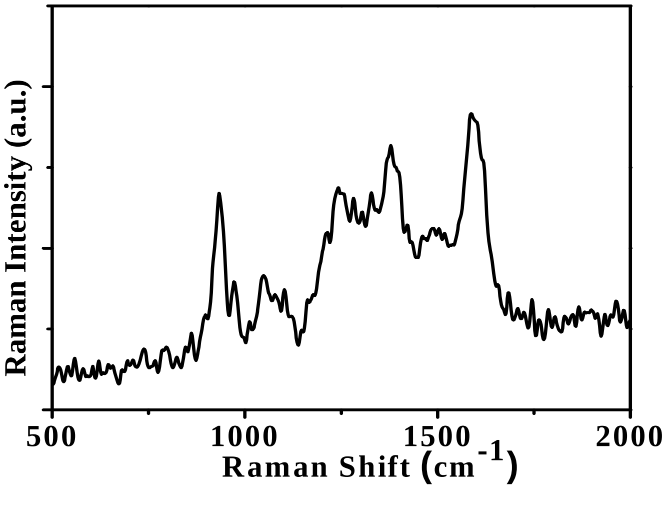

Fig. 6. FT-Raman spectroscopy of Polypyrrole thin film

The strong band located at approximately 1586 cm^{-1} represents the C=C backbone stretching of PPy [8, 9]. The double peaks at about 1046 and 1077 cm^{-1} are assigned to the C-H in plane deformation, i.e. one is representing the C–H in-plane bending associated radical cation and another is representing the C–H in-plane bending associated with dication [8]. The other peaks at approximately 1328 and 1378 cm^{-1} are attributed to the ring-stretching mode of

PPy [9] i.e. C–N stretching vibrations [8] in polypyrrole. The bands located at about 932 and 971 cm^{-1} are shifted by small value from the earlier reported value which are assigned to the ring deformation associated with dication (bipolaron) and radical cation (polaron), respectively [8, 9]. The bands at 1370 cm^{-1} belonged to the ring stretching, which are assigned to the oxidized species of PPy according to the literatures [8-11].

3.5. UV-vis spectroscopy. The UV-Vis spectroscopy of polypyrrole thin film is shown in the Fig. 7. The UV-Vis spectrum of polypyrrole features two absorption bands. The broad one is above the 650 nm and another is narrow and centered at nearly 431 nm. The films displayed strong absorption peaks at 431 nm, assigned as transitions from the PPy valence band to an anti-bipolarons band. Intense, broad absorptions are also occurred. This broad absorption is attributed to electron transitions from the polypyrrole valence band to a second bipolarons band in the band gap [12].

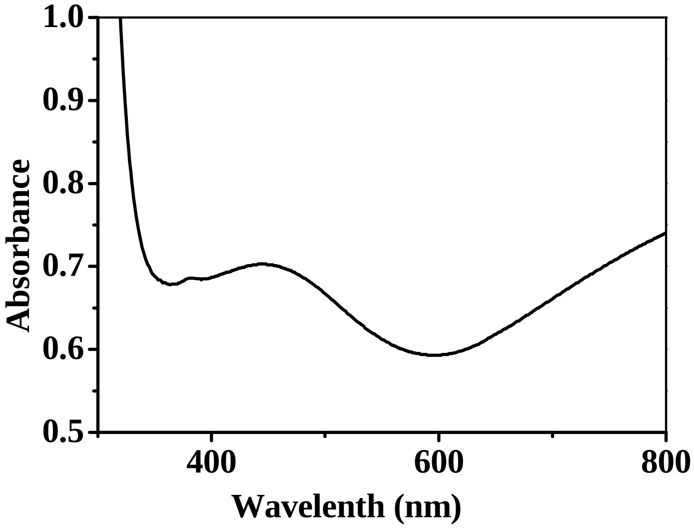

Fig. 7. UV-vis spectroscopy of Polypyrrole thin film.

3.6. Surface wettability study. The surface wettability properties are studied by means of Contact angle meter. As the number of deposition cycles increases the value of contact angle decreases from 48 deg to 30 deg shown in Fig. 8. The values of surface tension, surface energy and work of adhesion were calculated from the formulae as [13]:

$$\gamma_{sl} = \gamma_{lv} + \gamma_{sv} - 2\sqrt{\gamma_{lv}\gamma_{sv}}\,e^{-0.000125(\gamma_{lv}-\gamma_{sv})^2}, \tag{1}$$

$$\gamma_{sv} = \left[\gamma_{lv} + \frac{1}{4\beta\gamma_{lv}}\sec^4\left(\frac{\theta}{2}\right)\right] \pm \sqrt{\left[\gamma_{lv} + \frac{1}{4\beta\gamma_{lv}}\sec^4\left(\frac{\theta}{2}\right) - \frac{1}{2\beta}\right]^2 - \gamma_{lv}^2}, \tag{2}$$

$$W_a = \gamma_{sv} + \gamma_{lv} - \gamma_{ls}, \tag{3}$$

where, γ_{sl} is the surface tension in mN/m, γ_{sv} is the surface energy in $\mathrm{mJ/m^2}$, γ_{lv} is the surface tension of water which is equal to 71.99 mN/m [13], and $\mathrm{W_a}$ is the work of adhesion in $\mathrm{mJ/m^2}$.

The calculated values are summarized in the table 1. As the deposition cycles increases the value of surface tension goes on decreases from 19.60 mN/m to the 11.68 mN/m. This is due to formation of amorphous nature of chemically synthesized polypyrrole thin film.

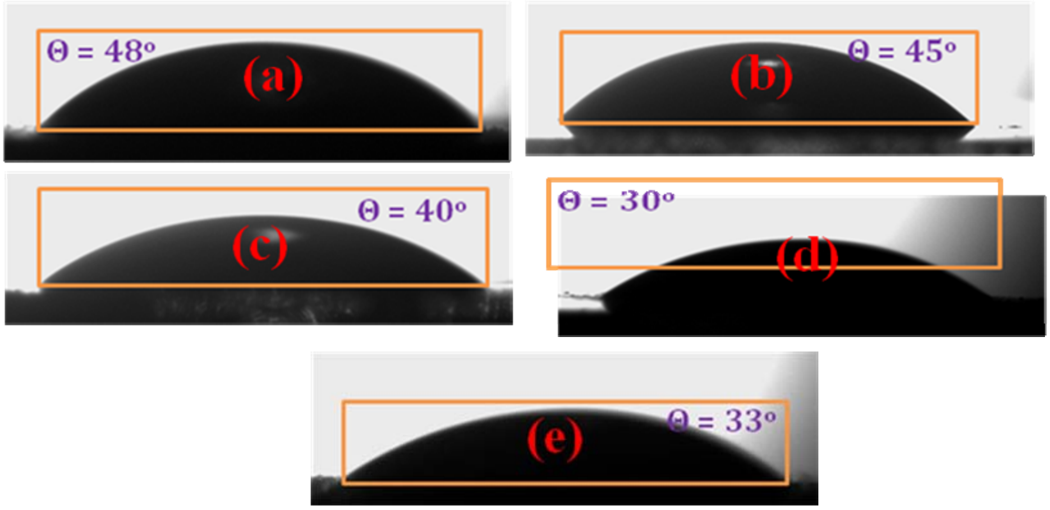

Fig. 8. Surface wettability study.
(a) Contact angle of PPy thin film deposited at 5 deposition cycles,
(b) Contact angle of PPy thin film deposited at 10 deposition cycles,
(c) Contact angle of PPy thin film deposited at 15 deposition cycles,
(d) Contact angle of PPy thin film deposited at 20 deposition cycles,
(e) Contact angle of PPy thin film deposited at 25 deposition cycles.

Table 1. Comparative study of thermodynamic surface parameter.

Deposition cycle	Contact angle ± 2	Surface tension γ_{sl}, mN/m	Surface energy γ_{sv}, mJ/m^2	Work of adhesion W_a, mJ/m^2
5	48°	19.60	26.21	78.60
10	45 °	18.02	26.81	80.78
15	40 °	15.98	27.65	83.66
20	30 °	11.68	28.97	89.28
25	33 °	13.04	28.65	87.60

4. Conclusions

In conclusion, the water insoluble Ppy was successfully synthesized by SILAR (Successive Ionic Layer Adsorption and Reaction) method. The synthesized polypyrrole are amorphous and hydrophilic in nature. The deposition cycles controls the thickness, contact angle, surface energy and work of adhesion. The FTIR and FT-Raman spectrum gives the detail information of polypyrrole structure. The formation of polaron and bi-polaron states of polymer film was confirmed by UV-Vis spectroscopy.

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